* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the manufacturing method of the laminate sheet manufactured with an application-of-pressure hot-forming device. It is related with the manufacturing method of the flexible laminated sheet especially used for an electronic electric appliance etc.
[0002]
[Description of the Prior Art]In recent years, in connection with the weight saving of an electronics product, a miniaturization, and densification, the demand of printed circuit boards becomes high and the demand of the flexible printed circuit boards which form a copper foil circuit on an insulation film especially is increasing. There are a laminate sheet (it expresses a heat-hardened type laminate sheet hereafter) on which the metallic foil was stuck by thermosetting adhesives, such as thermosetting resin, and a laminate sheet (it expresses a thermal melting arrival type laminate sheet hereafter) stuck by thermal melting arrival type adhesives, such as thermoplastics, in this flexible laminated sheet. After forming heat-hardened type adhesives, such as an epoxy resin and an acrylic resin, in both sides of heat-resistant films, such as a polyimide film, and pasting together to a metallic foil, a heat-hardened type laminate sheet performs a cure for a long time, makes hardening complete, and is produced. The lead-free solder which is an elevated temperature comes to be used for a solder material from the conventional melting point from an environmental problem, it becomes what has the still severer heat resistance required of a flexible laminated sheet in connection with it, and it is impossible in recent years, to be satisfied with the epoxy resin of this glue line, and an acrylic resin of heat resistance.
[0003]The thermal melting arrival type laminate sheet which uses thermoplastic polyimide for a glue line is used in order to meet the heat-resistant demand. Manufacture of a thermal melting

arrival type laminate sheet polyimide resin on one side of a metallic material Spreading and desiccation, Or the method of pasting a polyimide precursor solution together with a laminating device in spreading and desiccation, and the state where it carried out to carry out a cure and oppose adhesion sides, and manufacturing a double-sided flexible laminated sheet, Spreading, desiccation, and a cure make spreading and desiccation, or a polyimide precursor solution both sides of heat-resistant films, such as a polyimide film, for polyimide resin, produce an adhesive film, and with the composition of copper foil / adhesive film / copper foil. There are a method of pasting together with a laminating device and manufacturing a double-sided flexible laminated sheet, etc.

[0004]

[Problem(s) to be Solved by the Invention]When manufacturing the above-mentioned heat-hardened type laminate sheet, application-of-pressure hot-forming temperature is 200 ** or less in most cases. In cooking temperature of this level, the heat stress concerning laminated material is small, and it is hard to generate appearance defects, such as wrinkles at the time of a heat lamination.

[0005]However, when manufacturing a thermal melting arrival type laminate sheet, if application-of-pressure heating is not performed at the temperature more than the glass transition temperature (it expresses Tg) of the thermoplastics which constitutes a glue line, thermal melting arrival is not made. On the other hand, since the laminate sheet for electronic electric appliances receives heating at high temperature in process of component mounting, the thermoplastics which constitutes a glue line is asked for not less than at least 180 ** Tg. For the thermal melting arrival, the heat lamination temperature of not less than 200 ** is needed. In the lamination in such an elevated temperature, change of the thermal expansion and heat contraction of laminated material becomes large, and the laminated layered product has a problem of being easy to produce appearance defects, such as wrinkles.

[0006]If the generation cause of wrinkles is explained in more detail, when it laminates copper foil and thermoplastic polyimide with a heat roll laminating machine, copper foil and thermoplastic polyimide are stuck by passing through between the press rolls of a heat pressing state of a heat roll laminating machine. Although each laminated material is in the state where it expanded with heat, at the time of a lamination, since the coefficient of linear expansion of thermoplastic polyimide is larger than the coefficient of linear expansion of copper foil, generally the heat lamination of the thermoplastic polyimide is carried out with copper foil in the state where it was extended more greatly [a plane direction] than copper foil. And material holds heat also immediately after the lamination by which a pressure is opened wide, Since the temperature is higher than Tg of thermoplastic polyimide, thermoplastic polyimide is in a flow state, by cooling this rapidly, thermoplastic polyimide is contracted more greatly [a plane direction] than copper foil, and the made laminate sheet produces wrinkles in

a plane direction.

[0007]

[Means for Solving the Problem]This invention prevents generating of wrinkles at the time of laminating a heat-resistant adhesive film and a metallic material, and producing a flexible laminated sheet in view of said problem, and provides a method of raising productivity.

[0008]That is, this invention persons added a metallic roll whose cooking temperature is lower than a metallic roll of the preceding paragraph to the latter part of a metallic roll of the preceding paragraph of a heat roll laminating device, and found out that wrinkles made to a flexible laminated sheet could be reduced by laminating continuously. When it says in detail, with the 1st step of metallic roll (it is also called this laminate roller), a heat-resistant adhesive film and a metallic material are heated and pressurized, and laminate. A heat-resistant adhesive film and a metallic material are then stuck in the state where it was lengthened, by heating of a laminate roller. Since stretch amounts from a time which is ordinary temperature since coefficients of linear expansion differ differ and it is pasted together in the state, each material produces wrinkles in a flexible laminated sheet made from a difference in the amount of shrinkage of a heat-resistant adhesive film and a metallic material, when it returns to ordinary temperature rapidly. At this time, a metallic roll after the 2nd step that is temperature lower than this lamination temperature performs an annealing lamination (a metallic roll after the 2nd step is also called annealing laminate roller below) immediately after the 1st step of this lamination, By cooling gradually, pressurizing to temperature near Tg of a heat-resistant adhesive film eventually, it found out not producing wrinkles in a flexible laminated sheet.

[0009]Therefore, claim 1 of this invention is a manufacturing method which pastes a metallic foil and a heat-resistant adhesive film together using a heat roll laminating device which has at least two or more pairs of metallic rolls, and produces a heat-resistant flexible laminated sheet, It is a manufacturing method of a heat-resistant flexible laminated sheet, wherein cooking temperature of this metallic roll differs, respectively. Claim 2 is a manufacturing method of the heat-resistant flexible laminated sheet according to claim 1, wherein not less than 50 ** of cooking temperature of each metallic roll differs. Claim 3 is a manufacturing method of a heat-resistant flexible laminated sheet indicated in any 1 paragraph of claim 1, wherein cooking temperature of a metallic roll of a last stage of said heat roll laminating device is the following (glass transition temperature of +30 ** of a heat-resistant adhesive film) thru/or claim 2. Claim 4 is a manufacturing method of a heat-resistant flexible laminated sheet indicated in any 1 paragraph of claim 1, wherein diameters of two or more pairs of metallic rolls of said heat roll laminating device differ thru/or claim 3. When claim 5 pastes a metallic foil and a heat-resistant adhesive film together using said heat roll laminating device, it is a manufacturing method of a heat-resistant flexible laminated sheet indicated to a claim thru/or claim 4 arranging a protective material between a pressurization face of this device, and laminated material.

Application-of-pressure hot forming according [claim 6] to a metallic roll of the 1st step of said heat roll laminating device is performed above 200 **, And it is a manufacturing method of a heat-resistant flexible laminated sheet indicated in any 1 paragraph of claim 1 sticking a protective material and laminated material lightly and exfoliating this protective material from a laminate sheet after cooling thru/or claim 5. Here, a protective material puts a non-component of a laminate sheet. A protective material and laminated material are in the state where it was lightly stuck by passing a laminate roller. If the state of calling it adhesion lightly here says the state where both sides do not exfoliate and removes it by hand in the state where a protective film and laminated material apply no power, it will say the state of separating simply.

[0010]Claim 6 is a manufacturing method of a heat-resistant flexible laminated sheet indicated in any 1 paragraph of claim 1 using an adhesion sheet which contains thermoplastic polyimide 50% of the weight or more into adhesion components as said heat-resistant adhesive film thru/or claim 5. Claim 7 is a manufacturing method of a laminate sheet indicated in any 1 paragraph of claim 1 characterized by thickness using copper foil of 50 micrometers or less as said metallic material thru/or claim 6. Claim 8 is a manufacturing method of a laminate sheet indicated in any 1 paragraph of claim 1 characterized by using a polyimide film as said protective material thru/or claim 7.

[0011]

[Embodiment of the Invention]Hereafter, the details of this invention are explained.

[0012]Although the use in particular of the laminate sheet obtained with the manufacturing method of this invention is not limited, it is used mainly as a flexible laminated sheet for electronic electrical and electric equipment.

[0013]Although the film etc. with which the resin which has thermal melting arrival nature was impregnated are mentioned to substrates, such as a monolayer film which comprises the resin which has thermal melting arrival nature as a heat-resistant adhesive film, two or more layer film which forms the resin layer which has thermal melting arrival nature in the both sides of the core layer which does not have thermal melting arrival nature, paper, and glass fabrics, The monolayer film which comprises the resin which has thermal melting arrival nature as an adhesive film for flexible laminated sheets, and two or more layer film which forms the resin layer which has thermal melting arrival nature in the both sides of the core layer which does not have thermal melting arrival nature are more preferred than flexibility is inferior if a substrate with rigidity, such as glass fabrics, is used. What has heat resistance as the monolayer film which comprises the resin which has thermal melting arrival nature, and two or more layer film which forms the resin layer which has thermal melting arrival nature in the both sides of the core layer which does not have thermal melting arrival nature is preferred. That to which adhesion components, such as a resin layer which has the thermal melting arrival nature in an adhesive film, change from a thermoplastic polyimide system ingredient, for example,

thermoplastic polyimide, thermoplastic polyamidoimide, thermoplastic polyether imide, thermoplastic polyester imide, etc. may be used suitably. The use of the adhesive film which was preferably used for this invention and blended an epoxy resin, thermosetting resin like an acrylic resin, etc. of the adhesive film in which these heat-resistant thermoplastics is contained in adhesion components not less than 50% is also preferred. Various additive agents may be blended with the adhesive film for improvement in the various characteristics. For example, if it is for a surface slide nature improvement of a film, bulking agents, such as a filler, can be used, and the kind in particular will not be limited, but fillers, such as calcium hydrogen phosphate, can be used.

[0014]As long as the composition of an adhesive film has a heat-resistant glue line outside, the monolayer which comprises only the adhesion components of thermal melting arrival nature may be sufficient as it, but its film of the three-tiered structure which has a glue line of thermal melting arrival nature from viewpoints of the size characteristic etc. on both sides of the core layer which does not have thermal melting arrival nature is preferred. Especially if the core layer which does not have this thermal melting arrival nature has heat resistance, it will not be limited, but its use of the polyimide film of non-thermoplasticity is preferred.

[0015]Although not limited in particular for the manufacturing method of an adhesive film, when consisting of an adhesives layer monolayer, a film can be produced with the belt cast method, an extrusion method, etc. When the composition of an adhesive film consists of three layers called the core layer/glue line which does not have a glue line / thermal melting arrival nature, Thermal melting arrival nature to both sides of the core layer (for example, heat-resistant film) which it does not have adhesives, There are a method of applying to every [one side] or double-sided coincidence, and producing the adhesion sheet of three layers and the method of arranging and pasting together to both sides of a heat-resistant film the adhesive film of the monolayer which consists only of adhesion components, and producing the adhesive film of three layers. How to perform imide-ization in the method of applying adhesives and producing the adhesive film of three layers while applying to a heat-resistant film in the state of polyamic acid and making it dry subsequently when using especially the adhesives of a polyimide system, Soluble polyimide resin is then applied, there is the method of drying, and the method in particular of forming an adhesives layer is not asked. In addition, each resin of the core layer/glue line which does not have a glue line / heat-resistant weld nature is co-extruded, and there is also the method of producing a heat-resistant adhesive film at once.

[0016]Especially as a metallic material, although not limited, in the case of the laminate sheet used for electronic electric appliances, it is preferred to use copper foil from a point of conductivity and cost. About the thickness of a metallic foil, since thinning of the line width of a circuit pattern can be carried out so that the thickness of copper foil is thin, copper foil of 50 micrometers or less is preferred. Especially, since copper foil of 35 micrometers or less tends

to produce wrinkles when it is limp compared with copper foil of the thickness beyond it and a heat lamination is carried out, this invention demonstrates a prominent effect about copper foil of 35 micrometers or less. As a kind of copper foil, rolled copper foil, electrolytic copper foil, HTE copper foil, etc. are mentioned, there is no restriction in particular, and adhesives may be applied to these surfaces.

[0017]About a heat roll laminating device, laminated material is heated, and especially if it is a device which applies and laminates a pressure, it will not be scrupulous. About a heating method, especially if it can heat at a predetermined temperature, it will not be scrupulous, and a heat-medium-circulation method, a hot wind heating method, a dielectric-heating method, etc. are held. Although not less than 200 ** of cooking temperature is preferred, when the use which passes through the solder reflow oven of 240 ** of ambient temperature is presented with a laminate sheet for electronic packaging, in order to use the thermal melting arrival sheet which has Tg according to it, heating at not less than 240 ** is preferred. Although at least two or more pairs of metallic rolls are used in this invention, the laminate roller of construction material other than metallic rolls, such as rubber, may be used if needed. Especially if a predetermined pressure can be applied also about a pressurized system, it will not be scrupulous, and an oil hydraulic system, a pneumatic pressure method, the pressure method between gaps, etc. are held, and a pressure in particular is not limited.

[0018]As for the composition of a laminate roller, two or more pairs are preferred, and it is preferred to cool gradually the flexible laminated sheet which lowered gradually the cooking temperature of 1 to 1 pair of each laminate rollers, and laminated it. If it says in detail, in the 1st step of this laminate roller at the temperature more than Tg of a heat-resistant adhesive film. Can pressurize and heat, and make it weld to a metallic material, and the 2nd step of annealing laminate roller is continuously pressurized and heated at a temperature lower than this laminate roller, The 3rd step of annealing laminate roller is pressurized and heated at a temperature lower than the 2nd step of annealing laminate roller, and as for the temperature of the annealing laminate roller of a last stage, since it fixes from the flow state of a heat-resistant adhesive film, it is preferred that it is the following (Tg+30 ** of a heat-resistant adhesive film). Since the adhesion components of a heat-resistant adhesive film are still in a flow state as the temperature of the annealing laminate roller of a last stage is more than it, minute wrinkles will be produced in the made flexible laminated sheet. Although what times the temperature gradient of this laminate roller and an annealing laminate roller may be, necessity of tens of steps of laminate rollers will be carried out to it being several ** difference from this lamination to Tg+30 ** of a heat-resistant adhesive film, and cost starts also in equipment. Practical, as for the temperature gradient of this laminate roller and an annealing laminate roller, it is preferred that it is not less than 50 **, and, also as for the number of stages of the laminate roller, 2-5 steps are preferred in respect of cost.

[0019]It is important to pass an annealing laminate roller, pressurizing in an annealing lamination. By cooling slowly, generating of wrinkles can be prevented more, pressurizing. As for the pressure at this time, mm is preferred in 15Ns/mm - 75Ns /. Although it is not scrupulous and the diameter in particular of an adjoining laminate roller is not scrupulous, either, since the way where diameters differ can install especially the diameter of a laminate roller in contiguity more, it is preferred.
[0020]Although a protective material may not be used, you may use it in order to control the generation of crease etc. of the product laminated further. When using a protective material, it is [anything] good if it fills protecting from appearance defects, such as a generation of crease etc. of the laminated product. However, when the temperature at the time of processing can be borne and it processes [for example,] it at 250 **, the polyimide film etc. which have the heat resistance beyond it are effective. Although the thickness in particular of a protective material is not limited, a thickness of the purpose of controlling wrinkles formation of the laminate sheet after a lamination to not less than 50 micrometers is preferred. Since wrinkles formation can be controlled nearly thoroughly if the thickness of a protective material is not less than 75 micrometers, it is still more desirable. The protective material does not need to perform a surface treatment in particular etc., if it sticks lightly with laminated material. Conversely, when protective materials are laminated material and a thing which is not stuck, a surface treatment which is lightly stuck to the protective material side may be performed, the same surface treatment as the copper foil side may be performed, or a surface treatment may be performed to both a protective material and copper foil. If it seems that a protective material and laminated material stick lightly even if it is surface treatments performed for other purpose, such as rust prevention treatment performed in order to prevent oxidation of a copper foil surface, it will not matter even if it has performed the surface treatment.
[0021]The temperature of the laminate sheet at the time of exfoliating a protective material has a preferred temperature below the Tg, when using thermoplastics as a laminated material. They are a more desirable temperature lower not less than 50 ** than Tg and a still more desirable temperature lower not less than 100 ** than Tg. When most preferably cooled to a room temperature, it is preferred to exfoliate a protective material from a laminate sheet. An example is indicated below and this invention is explained more to details.
[0022]
[Example]Although the example and comparative example of this invention are given and this invention is explained in detail, this invention is not limited to these examples. Hereafter, in the example and the comparative example, the physical properties of an adhesives layer and the physical properties of the flexible substrate were measured as follows. According to JIS C6471 "6.5 Peel strength", peel strength produced the sample, exfoliated the copper foil portion of 5-mm width on condition of 50 mm/min at the exfoliation angle of 180 degrees, and measured

the load. The appearance state of the flexible laminated sheet was visually judged by the following standards.

O .. per [without Siwa] O****1 m^2 -- wrinkles -- in a five or more (examples 1-11) piece heat-resistant adhesive film, wrinkles per five or less pieces x ****1 m^2 per three or less ** ****1 m^2 per one or less O ****1 m^2. [wrinkles] [wrinkles] (Where a metallic material (Japan Energy 18-micrometer rolled-copper-foil BHY-22 B-T) is arranged on the both sides of Kaneka 142 [25 micrometer thickness PIXEO BP HT-] and Tg190 **) With drawing 1 - a heat roll laminating device like drawing 11, it laminated on condition of the lamination temperature shown in Table 1, the lamination pressure of 50Ns/mm, and lamination speed 2.0 m/min, and the flexible laminated sheet was obtained. As a result, the flexible laminated sheet which wrinkles do not have in appearance and is satisfactory as for peel strength was obtained. It is shown in Table 1 for details.

[0023]

[Table 1]

		実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9	実施例10	実施例11
ラミネート装置		図1	図2	図3	図4	図5	図6	図7	図8	図9	図10	図11
ラミネートロール温度(℃)	4a	350	350	350	350	350	350	350	350	350	350	350
	4b	200	200	250	250	250	300	300	300	310	300	300
	4c	—	—	200	200	200	250	250	250	270	250	250
	4d	—	—	—	—	—	200	200	200	230	200	200
	4e	—	—	—	—	—	—	—	—	200	150	150
保護フィルム		なし	なし	なし	なし	なし	なし	なし	なし	なし	なし	なし
フレキシブル積層板の外観状態		△	△	○△	○△	○△	○	○	○	○	◎	◎
剥離強度（N/cm）		12	12	12	12	12	12	12	12	12	12	12

(Examples 12-14) A metallic material (Japan Energy 18-micrometer rolled-copper-foil BHY-22 B-T) is arranged on the both sides of a heat-resistant adhesive film (Kaneka 142 [25 micrometer thickness PIXEO BP HT-], 190 Tg(s)), Where a protective material (Kaneka APIKARU 125AH) is furthermore arranged on the both sides, with drawing 12 - a heat roll laminating device like drawing 14, it laminated on condition of the lamination temperature shown in Table 1, the lamination pressure of 50Ns/mm, and lamination speed 2.0 m/min, and the flexible laminated sheet was obtained. As a result, the flexible laminated sheet which wrinkles do not have in appearance and is satisfactory as for peel strength was obtained. It is shown in Table 2 for details.

(Comparative examples 1 and 2) Using the same material as Example 1, with a heat roll laminating device like drawing 15, it laminated on condition of the lamination temperature shown in Table 1, the lamination pressure of 50Ns/mm, and lamination speed 2.0 m/min, and

the flexible laminated sheet was obtained. As a result, although peel strength was satisfactory, wrinkles occurred in the direction of movement of a lamination. It is shown in Table 2 for details.

[0024]

[Table 2]

		実施例 12	実施例 13	実施例 14	比較例 1
ラミネート装置		図12	図13	図14	図15
ラミネートロール温度(℃)	4a	350	350	350	350
	4b	200	200	250	−
	4c	−	−	200	−
	4d	−	−	−	−
	4e	−	−	−	−
保護フィルム		あり	あり	あり	なし
フレキシブル積層板の外観状態		○△	○	○	×
剥離強度（N/cm）		12	12	12	12

[0025]

[Effect of the Invention]by this invention, the productivity of the flexible laminated sheet in a heat roll laminating device can be boiled markedly, and can be raised. Therefore, this invention provides a material suitable as a flexible laminated sheet for electronic electric appliances especially.

[Translation done.]